POLYFIBROBLAST: A SELF-HEALING AND GALVANIC PROTECTION ADDITIVE

Progress Report #7

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14. ABSTRACT

The goal of this project is to develop a primer additive that mimics the self-healing ability of skin by forming a polymer scar across scratches. Designed to work with existing military grade primers, Polyfibroblast consists of microscopic, hollow zinc tubes filled with a moisture-cured polyurethane-urea (MCPU). When scratched, the foaming action of a propellant ejects the resin from the broken tubes and completely fills the crack. No catalysts or curing agents are needed since the polymerization is driven by ambient humidity.

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1 Summary

This month marked the transition to a pair of new strategies for improving the corrosion protection afforded by Polyfibroblast. With respect to self-healing, we screened a large number of silane-enhanced recipes for processability. With respect to galvanic protection, we blended zinc dust with solid polymer spheres to determine whether the packing mismatch impaired the ability to cathodically protect steel. We rounded out the month by exploring advances in drying that could potentially bring down processing costs and enhance scalability.

2 Project Goals and Objectives

Work continues to improve the corrosion protection performance through the end of the year. The more immediate tasks, however, involve the two remaining milestones: (1) shelf life will be sufficient to survive one week at 100°F and 100% relative humidity without loss of liquid volume fraction by mid August, and (2) PPG will demonstrate the capability to synthesize enough Polyfibroblast filler to make 1-gallon batches of primer by early September.

3 Key Accomplishments

3.1 Silane Formulation Processability

Silane coupling agents may be added to the existing microcapsules either in low concentrations, in which they serve primarily as a wetting agent for the polyurea, or in high concentrations, in which they form the primary moisture barrier layer. The choice for the final formulation depends in large measure on the one that provides the best corrosion potential, but it is constrained by the need to form stable microcapsules. To this end, we explored a number of recipes in which the following silane coupling agents were substituted for isophorone diisocyanate (IPDI) in varying concentrations ranging from 1 to 70%

- Octadecyltrimethoxy silane (OTS)
- Isocyanatopropyltrimethoxy silane (ITS).
- Glycidoxypropyltrimethoxy silane (GPS)

As expected, the lowest concentrations most readily formed stable microcapsules. The more polar silanes (ITS and GPS), in particular, could not be microencapsulated above 5% (w/w) silane. This finding is not surprising, and likely results from the polar silane molecules segregating to the interface, where they prevent the formation of a dense polymer skin layer.

OTS has been shown to encapsulate up to 20% (w/w) with no issues. At 70% OTS, the isocyanate monomers are no longer completely miscible with the OTS. This issue has been addressed by substituting poly(phenylene isocyanate) (PPI) with toluene diisocyanate (TDI), which allows microencapsulation to occur.

Table I: *Table summarizing the different attempts to incorporate silane coupling agents into microcapsules. Notably, GPS and ITS could not be encapsulated above a concentration of 5% (w/w). OTS incorporated more readily, but required formulation changes above 50% OTS to address miscibility issues with the isocyanate monomers at those concentrations.*

Formulation						
Silane Type	% Silane	Silane (g)	IPDI (g)	MIL-P (g)	PPI (g)	Description of Microcapsules
GPS	1	0.2	16.8	1	2	Well formed microcapsules, which had a liquid interior. Pass
GPS	S	1.0	16.0	1	2	Well formed microcapsules, which had a liquid interior. Pass
GPS	10	2.0	1S.0	1	2	Poorly formed microcapsules with no liquid interior. Fail
GPS	20	4.0	13.0	1	2	Microcapsules never settled and the solution turned into a foam. Fail
GPS	50	10.0	7.0	1	2	Microcapsules never settled and the solution turned into a foam. Fail
GPS	70	14.0	3.0	1	2	Microcapsules never settled and the solution turned into a foam. Fail
ITS	1	0.2	16.8	1	2	Well-formed microcapsules with noticeable internal structure. Pass
ITS	S	1.0	16.0	1	2	Well formed microcapsules, which had a liquid interior. Pass
ITS	10	2.0	1S.0	1	2	Microcapsules never settled and the solution turned into a foam. Fail
ITS	20	4.0	13.0	1	2	Well-formed microcapsules, but with no liquid interior. Fail
ITS	50	10.0	7.0	1	2	Poorly formed microcapsules with no liquid interior. Fail
ITS	70	14.0	3.0	1	2	Poorly formed microcapsules with no liquid interior. Fail
OTS	1	0.2	16.8	1	2	Well-formed microcapsules with noticeable internal structure. Pass
OTS	5	1.0	16.0	1	2	Well-formed microcapsules with noticeable internal structure. Pass
OTS	10	2.0	1S.0	1	2	Well-formed microcapsules with noticeable internal structure. Pass
OTS	20	4.0	13.0	1	2	Well-formed microcapsules with noticeable internal structure. Pass
OTS	50	10.0	7.0	1	2	Well-formed microcapsules with noticeable internal structure. Pass
OTS	70	14.0	3.0	1	2	PPI was not soluble in the OTS. Microcapsules reaction was halted. Fail

3.2 Zinc Dust Filler

Perhaps the greatest teehnieal ehallenge faeing this program in FY11 has been the need to reaeh levels of galvanic protection that are aehieved by off-the-shelf zine-rich primers. Despite our ability to heal seratehes up to 1/8th in., some ineomplete healing is unavoidablc. These regions corrode at a faster rate than comparable scratches in a zinc-rich primer. Previous electrochcmical charaeterization of the Ni/Zn shell of Polyfibroblast showed that while the alloy afforded some galvanie protection, the protection was temporary.

Rather than pouring resourees into furthcr Ni/Zn alloy development, a better approaeh was to substitute some fraction of Polyfibroblast microcapsules for zinc dust instead. The zine dust approach overeomes the main limitations of relying solely upon the Ni/Zn shell for galvanie protection:

1. Eleetroless plating may not physieally allow suffieiently high zinc concentrations to avoid the reversal of polarization at long times.
2. While electroless plating is praetical for thin films at the pilot scale, it may not be eeonomieally sensible for generating tons of bulk saerificial zine.
3. Substituting zine dust for the mieroeapsules even brings down the eost due to the polymer component of the mieroeapsule.

The largest initial eoneern with blending zine dust and mierocapsules is that the microcapsules will interfere with the packing of the zinc dust. To this end, we blended zine dust with fully eured, solid polymer mieroeapsules with no metallie shell. The overall filler loading was fixed at 55% (vol/vol), the eritieal pigment volume eoneentration (CPVC). Within that 55%, the volume fraetion of zine powder was adjusted from 25% to 90%.

The solid spheres neither providc self-healing eapability nor galvanic protection, and in this ease, they do not even provide eleetrieal eonduetivity. The goal of this experiment is to sec if the 37 μm polymer spheres prevent the 7 μm zine partieles from forming a fully percolated network. If percolation is disrupted, it will be manifested as a reduction in the overall galvanie proteetion

capacity. Poorly packed zinc dust will no longer act as a single, large sacrificial anode, but rather as individual particles or small clusters, which will be more quickly consumed.

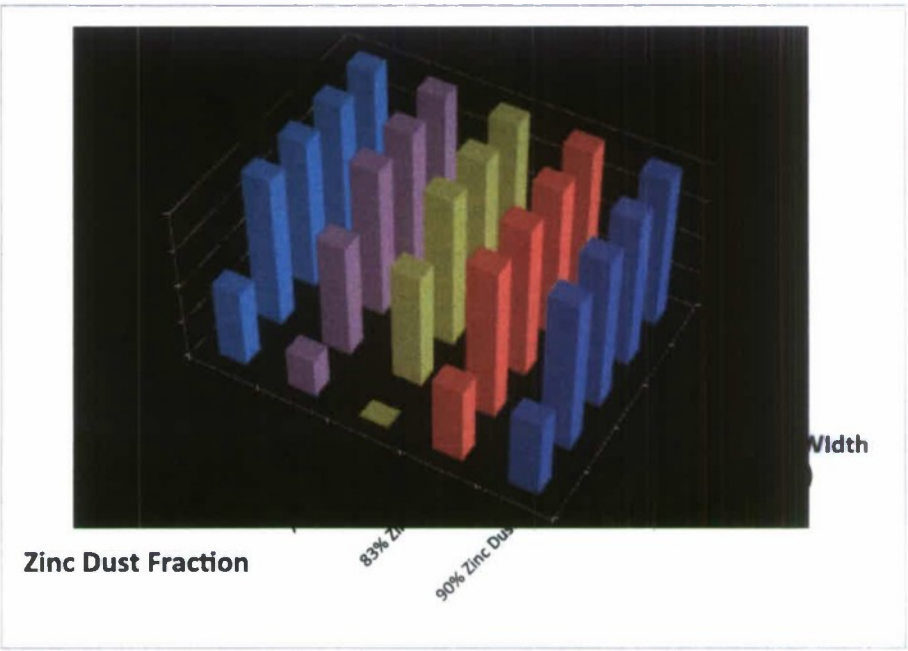

Figure 1: *Moisture resistance data for primers formed with zinc dust and uncoated polymer spheres. Galvanic protection was most effective for small scratches, but it was independent of zinc dust fraction.*

Figure 1 shows that galvanic protection was most effective in the thinnest scratches. The performance in the wider scratches was actually inferior to the self-healing microcapsules. However, the overall corrosion protection was independent of the ratio of zinc particles to polymer particles. Although this data suggests that the smaller zinc particles have no problem packing around the larger polymer spheres, the relatively poor performance in the larger scratches seems to indicate that perhaps the total filler loading was below the CPVC. These experiments will be repeated for a higher overall loading of filler material.

3.3 Processing Methodology

Spray drying was successfully tested at PPG on fully cured polymer spheres, as shown in Figure 2. The Buchi B-191 mini spray dryer operates by spraying a microcapsule slurry as a fine mist at 80°C. The high surface area of the droplets and elevated temperature serve to remove water before the microcapsules hit the ground. Moving forward, the main technical challenge is to limit the breakage of microcapsules during pumping, and to limit unwanted curing that might be expected in water at 80°C.

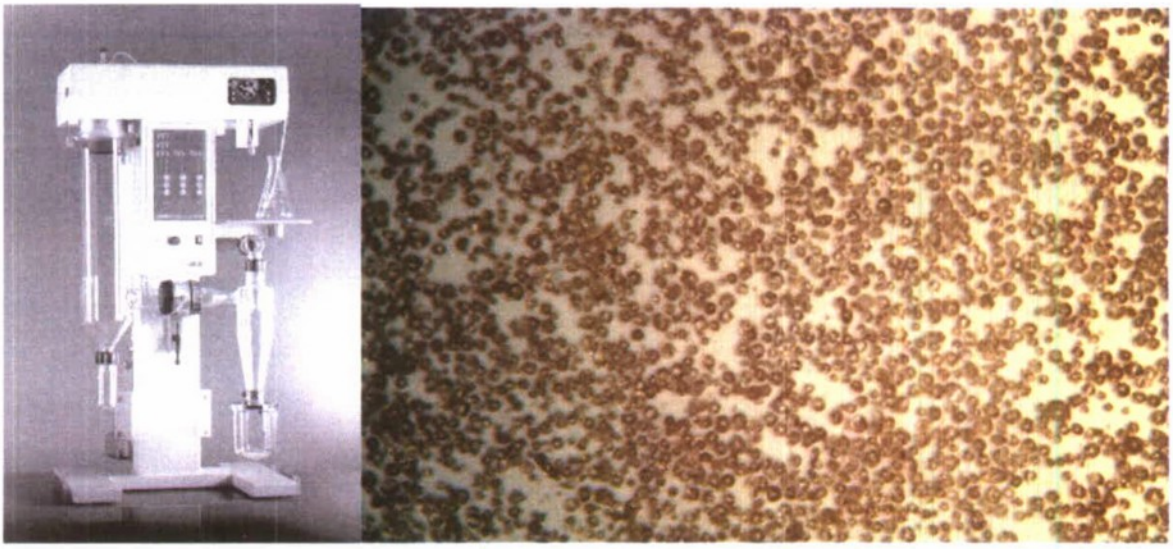

Figure 2: *(left) Bruchi B-191 mini spray dryer. (right) Free flowing solid microcapsules (~37μm diameter) dispersed by spray drying.*

4 Next Steps

4.1 PPG: Scale-Up, Drying, and Characterization

PPG has little over one month remaining to prepare for the final 1-gallon scale-up. Their exploration of alternative drying methods ties in to the scale-up effort, since freeze-drying the larger batch may not be possible. Finally, PPG will continue to characterize panels prepared at APL as needed.

4.2 APL: Silane Optimizations

In addition to continuing work on silane formulations and zinc dust incorporation, APL will also revisit the issue of shelf life by evaluating the current "best practice" microcapsule formulation after one week of exposure to water at 100°F.